

ELECTROCHEMISTRY / INTERFACIAL KINETICS

Q1. General Physical Chemistry I 2001, Question 5

For the reaction $\text{Ox} + e^- \rightleftharpoons \text{Red}$ at an electrode, the net current flowing, i , depends on the applied potential E :

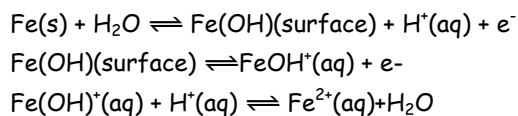
$$i \propto -[\text{Ox}] \exp\left\{\frac{-\alpha F}{RT}(E-E^\circ)\right\} + [\text{Red}] \exp\left\{\frac{\beta F}{RT}(E-E^\circ)\right\}$$

where E° is the standard potential of the redox couple, F is the Faraday constant, and α , β are transfer coefficients. The first term in the equation relates to the reduction of Ox; the second term to the oxidation of Red.

- a) Under what conditions can values of α and β be determined from plots of $\ln(|i|)$ against E ?
- b) For simple one-electron processes α and β commonly have values close to 0.5. For more complex, multi-electron reactions other values can arise which suggest a mechanism for the reaction. The rate of anodic (oxidative) dissolution of iron in 0.5 M $\text{FeSO}_4(\text{aq})$, 0.5 M $\text{Na}_2\text{SO}_4(\text{aq})$ has been studied at pH 3.0 and the following data obtained for the process $\frac{1}{2}\text{Fe}(\text{s}) \rightarrow \frac{1}{2}\text{Fe}^{2+}(\text{aq}) + e^-$

$(E-E^\circ)/\text{V}$	0.100	0.140	0.180	0.220
$ i / \text{Am}^{-2}$	1	10	100	1000

- i) Use a graphical procedure to determine a value of β for the process. (Note: $RT/F=25.69$ mV at 298 K)
- ii) The mechanism of the reaction is thought to be

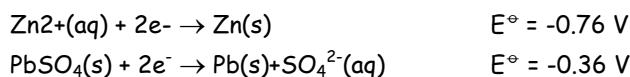


Use your value of β from part i) to deduce the rate determining step in this mechanism.

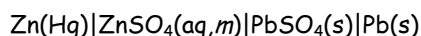
- iii) If the pH of the solution was increased by one unit, by what value would the current values alter?

Q2. General Physical Chemistry II 2001, Question 2

- a) Explain the term *standard electrode potential* with reference to the following half cell reactions.



- b) Explain why the *standard emf* of the cell



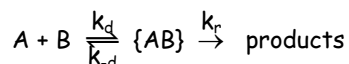
has a value close to +0.40 V at 298 K. The Zn(Hg) electrode is a saturated solution of Zn in Hg. Assume that ZnSO_4 is fully dissociated into $\text{Zn}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$.

- c) Write down the Nernst equation for the cell given in part b) when the molar concentration of zinc sulphate, assumed to be completely soluble in water, is m .

- d) Precise measurements at 298 K of the emf of the cell in part b) gave a value of +0.4085 V for the *standard* emf, and a value of +0.6114 V when $m=0.0005$ M. Calculate the mean activity coefficient of zinc sulphate at 0.0005 M. [Note $RT/F = 25.69$ mV at 298 K].
- e) Outline the factors responsible for differences between experimental values of the activity coefficients of ionic solutions and those predicted by Debye-Huckel theory.

Q3. General Physical Chemistry II 2000, Question 5

- a) A bimolecular reaction between two species A and B in solution can be envisaged as proceeding through an encounter pair {AB} according to the following mechanism:

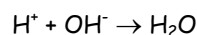


Explain how this mechanism leads to the concept of *diffusion-controlled* and *activation-controlled* reactions. What determines the temperature dependence of the rate constant in each case?

- b) The diffusion-controlled rate constant for reactions between neutral species in solution may be approximated by the Stokes-Einstein-Smoluchowski equation

$$k_d = \frac{8000RT}{3\eta} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$$

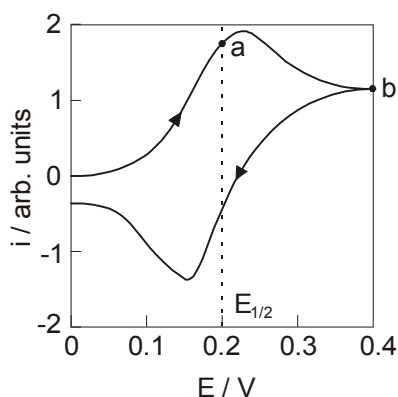
where η is the viscosity of the solvent in Pa s and RT is in Jmol^{-1} . The rate constant for the reaction



is found to be $1.4 \times 10^{11} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 298 K. Calculate a typical value of k_d from the Stokes-Einstein-Smoluchowski equation and comment on the rate constant for the $\text{H}^+ + \text{OH}^-$ reaction in the light of this value. [note: $\eta = 0.89 \times 10^{-3} \text{ Pa s}$ for water at 298 K]

Suggest a method by which rate constants can be measured for reactions such as $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$.

- c) The figure below shows the first sweep of a cyclic voltammogram for the oxidation of species A to species A^+ at an electrode where the kinetics are fast ('reversible' electrode kinetics).



Explain the shape of the voltammogram. Include in your answer a sketch of the concentration profile of A and A^+ in solution at points a and b on the voltammogram. You may assume that initially $[A]=1.0$ and $[A^+]=0.0$ in arbitrary concentration units.

How would the voltammogram differ if the electrode reaction were slow ('irreversible' electrode kinetics)?

Q4. General Physical Chemistry I 1999, Question 4

For the reaction $\text{Ox} + e^- \rightleftharpoons \text{Red}$ at an electrode in an electrolytic cell, the net current flowing, i , can be shown to depend on the applied potential, E :

$$i \propto -[\text{Ox}] \exp\left\{\frac{-\alpha F}{RT}(E-E^\ominus)\right\} + [\text{Red}] \exp\left\{\frac{\beta F}{RT}(E-E^\ominus)\right\}$$

where E^\ominus is the standard potential of the redox couple, F is the Faraday constant, and α, β are transfer coefficients such that $\alpha + \beta = 1$. The first term in the equation relates to the reduction of Ox ; the second term to the oxidation of Red .

- a) Show that if data can be recorded at sufficiently positive or negative values of E such that one or other of the terms in the equation can be neglected, then values of α and β can be determined from plots of $\ln(|i|)$ against E .
- b) The following data were collected at a carbon electrode using a solution containing 0.10 M Ce(IV) and 0.010 M Ce(III) .

E / mV	1576	1556	1536	1436	1416	1396	1376
$10^6 i / \text{A}$	+350	+230	+150	-225	-250	-475	-725

- i) Why does the current change sign as the applied potential decreases?
- ii) By plotting $\ln|i|$ against E on a single graph estimate values of α and β for the Ce(IV)/Ce(III) couple.
- iii) Use the equation above to find an expression for the potential at which no current flow occurs in terms of E^\ominus and the concentrations $[\text{Ox}]$ and $[\text{Red}]$. Comment on the result.
- iv) Use the results of parts ii) and iii) to determine a value for E^\ominus for the Ce(IV)/Ce(III) couple.

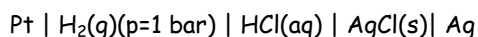
Q5. General Physical Chemistry II 1999, Question 6

- a) The Debye-Huckel limiting law for an aqueous solution of electrolyte at 298 K is

$$\log_{10} \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

where γ_{\pm} is the mean ionic activity coefficient, z_+ and z_- the ionic charges, and I the ionic strength. Summarise the physical model used in establishing the Debye-Huckel limiting law.

- b) Write down the cell reaction for the Harned cell

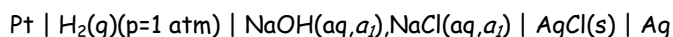


and obtain an expression for the EMF, E , assuming that the gas-phase species behaves ideally.

- c) The data given below show the EMF for the Harned cell at 298 K as a function of the molality, m , of the Cl^- ion. Using the Debye-Huckel law, determine the standard potential of the silver/silver chloride electrode.

$m / \text{mol kg}^{-1}$	0.003215	0.005619	0.009318
E / mV	520.63	492.57	468.60

- d) At 298 K the cell



has an EMF of 1.05080 V. Estimate the autoprotolysis constant (ionic product), K_w , of water at 298 K.